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(21) International Application Number: PCT/US95/13100 (22) International Filing Date: 6 October 1995 (06.10.95) (30) Priority Data: 08/319,212 6 October 1994 (06.10.94) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520 (US). (72) Inventors: HENDRIKSEN, Dan, Eldon; 3206 Brook Grove Drive, Kingwood, TX 77345 (US). LATTNER, James, Richardson; 4147 Crownwood, Seabrook, TX 77586 (US). ZBORAY, James, Andrew; 3809 Browning, Houston, TX 77005 (US). SOLED, Stuart, Leon; 21 Cooks Cross Road, Pittstown, NJ 08867 (US). (74) Agents: ZBORAY, James, A. et al.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).	(81) Designated States: AU, CA, JP, SG, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>	
(54) Title: PROCESS FOR MANUFACTURING ETHYLBENZENE OR CUMENE (57) Abstract <p>The production of ethylbenzene from dilute ethylene and dilute benzene is accomplished in three steps. First, the benzene feedstock stream, containing benzene, is alkylated with the dilute ethylene feedstock stream, containing ethylene, to form ethylbenzene along with polyethylbenzenes (PEB) which includes a mixture of di- and triethylbenzene that may also contain tetra-, penta-, and hexaethylbenzenes. Second, the product of the first step is distilled to remove the unreacted benzene and other unreacted material. Some of the ethylbenzene is recovered by distillation. In a third step, the polyethylbenzenes are transalkylated with excess pure benzene to form product ethylbenzene. The product ethylbenzene may be recovered by distillation. This process utilizing dilute benzene feedstock may also be applied to the manufacture of cumene, rather than ethylbenzene, by using a dilute propylene feedstock stream, rather than a dilute ethylene feedstock stream. Catalysts used for the alkylation and transalkylation step are supported heteropolyacid catalysts such as phosphotungstic acid on a silica support or Y zeolite catalyst in the acid form.</p>		

PROCESS FOR MANUFACTURING ETHYLBENZENE OR CUMENE

This invention relates to petroleum refining and petrochemistry, particularly to a process for manufacturing ethylbenzene from a composition containing benzene and another composition containing ethylene. Ethylbenzene is used commercially primarily as a raw material in the manufacture of styrene. This invention relates also to a process for manufacturing cumene from a composition containing benzene and another composition containing propylene. Cumene is used essentially as a raw material in the manufacture of phenol.

The known processes for the manufacture of ethylbenzene use the Friedel-Crafts reaction of alkylation of benzene by ethylene. Similarly, Friedel-Crafts reaction of alkylation of benzene by propylene is used to manufacture cumene.

The catalysts for this reaction are typically Bronsted or Lewis acids, including aluminum chloride, boron trifluoride deposited on alumina, or zeolites used in liquid or gas phase.

One of the difficulties encountered in using this reaction is that the ethylbenzene formed is more reactive than benzene with respect to ethylene, which leads to the production of diethylbenzenes, which are themselves more reactive than ethylbenzene, and therefore have a tendency to form triethylbenzenes.

To limit these polyalkylation reactions, the prior art teaches the use of a strong excess of benzene with respect to the ethylene at the entry of the alkylation reactors.

Thus, the benzene/ethylene molar ratio is generally between 2 and 2.5 for the processes using aluminum chloride, and the ratio may even reach a value between 8 and 16 for processes using zeolites in gas phase.

In all the known processes cited above, the benzene and the ethylene used in the alkylation reaction are each products of sufficient purity to lead to technical grade ethylbenzene, which can then be purified to the desired degree by distillation-rectification.

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Petroleum refining technologies and the principle products resulting from them have also been described in Encyclopedia of Chemical Technology, 3rd Edition, Vol. 17, p. 183 and following.

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Thus, certain heavy fractions obtained by distillation of petroleum are catalytically cracked in fluid catalytic cracking (FCC) to yield lighter products, which are put on the market as high-octane gasolines. This cracking also provides a certain proportion of so-called FCC gases, of which a light fraction comprises saturated hydrocarbons having two or fewer carbons and ethylene. This ethylene is present in a proportion by weight generally lower than 30% in this light fraction. The recovery of this ethylene by liquefaction followed by distillation is not profitable, and the use of this ethylene essentially diluted by methane and ethane has already been described, particularly in GB-1 013 268, US-A-3,131,230, US-A-3,200,164, and US-A-3,205,277.

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In the alkylation processes of these patents, the benzene/ethylene ratio is greater than 2 and is generally greater than the ratio used in the known processes involving practically pure ethylene, so that the ethylene present in this light fraction can be exhausted (see also: Process Economics Program, Stanford Research Institute, Report no. 33, October 1986, p. 37).

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The resulting alkylate is preponderant in benzene and includes a small quantity of ethylbenzene and polyethylbenzenes. This involves a significant cost for separating the ethylbenzene from this mixture. Thus, the light fraction of the FCC gases is not generally valued economically for its ethylene content.

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FCC

off gas

requiring ceramic lined vessels and expensive alloy materials of construction for most of the process equipment and creating many operational problems. Additionally, there is a significant environmental disposal problem associated with the use of aluminum chloride catalyst systems in benzene alkylation and transalkylation processes. The aluminum chloride catalyst operates in a once-through mode, and therefore the effluent from the process contains residual aluminum chloride and is often difficult to dispose of in an environmentally acceptable manner.

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In one example in WO 93/20029, a small-pore mordenite with the aluminum removed, and a Si/Al ratio of 25, is used as the catalyst for the alkylation step, but not the transalkylation step. A large amount of mordenite relative to the benzene is required to effect the alkylation reaction, possibly because mordenite has been reported to rapidly lose its activity during the alkylation of benzene by ethylene.

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Accordingly, it would be desirable to discover an alkylation catalyst system capable of functioning in the regime of impure ethylene and impure benzene described above and without the corrosion, environmental, and activity problems associated with the catalysts identified in the prior art as being efficient for this purpose.

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SUMMARY

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This invention provides a process for manufacturing ethylbenzene from a first stream containing benzene and a second stream containing ethylene, comprising:

very best definition

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- a) reacting said first stream with said second stream in an alkylation reaction of benzene by ethylene with a supported heteropolyacid or a Y zeolite catalyst to obtain a third stream consisting of an alkylate stream containing mono- and poly- ethylbenzenes in which the benzene ring to thyl group molar ratio, including

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In another embodiment of the process, the fourth stream, which comprises the distillate of step b) also contains monoethylbenzene, and this fourth stream undergoes at least one distillation-rectification to obtain an eighth stream comprising a head fraction containing
5 monoethylbenzene and a ninth stream comprising a tail fraction containing poly-ethylbenzenes.

In another embodiment of the process, the eighth stream comprising a head fraction containing monoethylbenzene is recycled to
10 step a) to cause alkylation of this monoethylbenzene into poly-ethylbenzenes.

In another embodiment of the process, a tenth stream comprising a gasoline fraction consisting of saturated hydrocarbons and with a majority
15 of the benzene removed is recovered by an additional distillation-rectification.

The above embodiments may be modified to produce cumene by substituting propylene for the ethylene.
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DETAILED DESCRIPTION

The production of ethylbenzene from dilute ethylene and dilute benzene is accomplished in three steps. First, the benzene feedstock
25 stream, containing benzene, is alkylated with the dilute ethylene feedstock stream, containing ethylene, to form ethylbenzene along with polyethylbenzenes (PEB) which includes a mixture of di- and triethylbenzene that may also contain tetra-, penta-, and hexaethylbenzenes. Second, the product of the first step is distilled to
30 remove the unreacted benzene and other unreacted material. Some of the ethylbenzene is recovered by distillation. In a third step, the polyethylbenzenes are transalkylated with excess pure benzene to form product ethylbenzene. The product ethylbenzene may be recovered by distillation.

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contained in the FCC gases from the refinery with all the benzene available in the light reformat.

5 In the first step, the two feedstock streams are brought together, under effective operating conditions, which are well known in the art, for the alkylation of benzene by the ethylene.

10 It is preferable for the benzene/ethylene molar ratio to be between 0.3 and 1 so that practically all the benzene put into reaction will be reacted with a sufficiently rapid rate of the alkylation reaction of benzene by ethylene.

15 It is preferable for the distillation rectification operation(s) or step b) to be regulated so that said distillate of step b) no longer contains mono-ethylbenzene, which is obtained by at least one distillation-rectification to obtain a head fraction with monoethylbenzene and a tail fraction with di- and tri-ethylbenzene and heavy elements.

20 Preferably, this head fraction containing mono-ethylbenzene is recycled in stage a) to bring about alkylation of this monoethylbenzene into di- and tri-ethylbenzene. In this way the alkylate coming from the alkylation reactor is richer in di- and tri-ethylbenzene than the alkylate obtained without recycling and the benzene contained in the benzene feedstock stream combines with a greater number of ethylene molecules;
25 it is a better carrier of the ethyl group in the transalkylation of step c).

30 Since the benzene feedstock stream is a light reformat, it is advantageous to recover in step b), by another distillation-rectification operation, a gasoline fraction formed of saturated hydrocarbons with a majority of the benzene removed.

35 Transalkylation of step c) of the process according to the invention is performed according to known processes, however the proportion of material undergoing transalkylation is greater than in conventional processes. The feed rate of benzene used is then adjusted to conform to customary ratios of benzene/ethyl groups. This transalkylation can be

First Step - Alkylation

In a 300 cc magnetically stirred autoclave were placed dry benzene (40.4 g), dry hexanes (59.0 g), and a catalyst composed of 30% by weight of phosphotungstic acid supported on silica powder (9.6 g) prepared as described above. The autoclave was sealed, purged with hydrogen to remove air, and then pressured with 50 psig of hydrogen. The autoclave was heated to 180°C with stirring and then an additional pressure of 15 psi of ethylene was added to the autoclave from a reservoir through a pressure regulator. As ethylene was consumed in the reaction more ethylene was added from the reservoir to maintain the pressure in the autoclave. After 17 hours the ethylene supply was closed, the reactor was cooled and vented, and the contents were removed. The amount of ethylene consumed was not directly measured.

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A second alkylation reaction was run in the same manner to duplicate the results and to make more product. The materials initially placed in the autoclave were dry benzene (41.0 g), dry hexanes (59.7 g), and 30% by weight of phosphotungstic acid supported on silica powder (9.7 g) prepared as described above. The reaction was run for 17.5 hours.

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The catalyst was filtered from the product of each reaction, and the products were combined and analyzed by capillary column gas chromatography. The combined product was found to contain 21.4 g of benzene and 62.4 g of ethylbenzene and polyethylbenzenes with the following composition by weight:

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<u>EB</u>	<u>di-EB</u>	<u>tri-EB</u>	<u>tetra-EB</u>	<u>penta-EB</u>	<u>hexa-EB</u>
34.3%	23.3%	13.8%	6.8%	8.3%	13.4%

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Thus, 73.7% of the benzene was converted. The mixture of ethylbenzene and polyethylbenzenes has a molar ratio of ethyl groups to benzene rings (Et/Bz) of 2.2. The Et/Bz molar ratio in the entire product, including unreacted benzene, is 1.4. The only difference between the two

by distillation in the second step is 74.3 g EB. Those skilled in the art will recognize that both the remaining polyethylbenzenes in the transalkylation product and the remaining excess benzene may be recovered and recycled to another transalkylation reaction to yield additional ethylbenzene.

Example 2

10 This Example illustrates the production of ethylbenzene using a Y zeolite catalyst in the acid form (LZY-84, UOP) for both reaction steps.

Alkylation Catalyst Preparation

15 This catalyst was received as 1/16 inch extrudates. Before use it was crushed to a powder and dried under vacuum at 200°C overnight. All other procedures except for the catalyst preparation are the same as in Example 1.

First Step - Alkylation

20 In a 300 cc magnetically stirred autoclave were placed dry benzene (42.2 g), dry hexanes (62.4 g), and a Y zeolite catalyst (LZY-84, UOP, 8.8 g) prepared as described above. The autoclave was sealed, purged with hydrogen to remove air, and then pressured with 50 psig of hydrogen. The autoclave was heated to 180°C with stirring and then an additional
25 pressure of 15 psi of ethylene was added to the autoclave from a reservoir through a pressure regulator. As ethylene was consumed in the reaction more ethylene was added from the reservoir to maintain the pressure in the autoclave. After 17.5 hours the ethylene supply was closed, the reactor was cooled and vented, and the contents were removed.

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 A second alkylation reaction was run in the same manner. The materials initially placed in the autoclave were dry benzene (43.8 g), dry hexanes (60.5 g), and Y zeolite catalyst (LZY-84, UOP, 7.8 g) prepared as described above. The reaction was run for 17.5 hours.

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ratio of 5.6. The autoclave was sealed, purged with nitrogen to remove air, and then pressured with 50 psig of nitrogen. The autoclave was heated to 180°C with stirring. After 20.7 hours the reactor was cooled and vented, and the contents were removed and analyzed by capillary
5 column gas chromatography. A yield of 33.0 g of ethylbenzene was found. Thus, transalkylation of the entire mixture of ethylbenzene and polyethylbenzenes remaining after distillation would yield 90.6 g of EB, which combined with the EB recovered by distillation in the second step, is 109.6 g EB. Those skilled in the art will recognize that both the
10 remaining polyethylbenzenes in the transalkylation product and the remaining excess benzene may be recovered and recycled to another transalkylation reaction to yield additional ethylbenzene.

- 5 a) reacting the first stream with the second stream in an alkylation reaction of benzene by ethylene using a Y zeolite catalyst to obtain a third stream consisting of an alkylate stream containing mono- and poly-ethylbenzenes in which the benzene ring to ethyl group molar ratio, including the unreacted benzene, in the alkylate stream, is equal to or less than 1.5;
- 10 b) subjecting this third stream consisting of an alkylate stream to at least one distillation/rectification to obtain a fourth stream which is a distillate containing poly-ethylbenzenes;
- 15 c) transalkylating this fourth stream consisting of the distillate with a fifth stream consisting of benzene using a Y zeolite catalyst to obtain a sixth stream consisting of a transalkylate rich in monoethylbenzene; and
- 20 d) subjecting this sixth stream consisting of a transalkylate to at least one distillation-rectification to obtain a seventh stream consisting of ethylbenzene.
- 25 3. A process for manufacturing ethylbenzene from a first stream containing benzene and a second stream containing ethylene, comprising:
- 30 a) reacting the first stream with the second stream in an alkylation reaction of benzene by ethylene with a supported heteropolyacid catalyst to obtain a third stream consisting of an alkylate stream containing mono- and poly-ethylbenzenes in which the benzene ring to ethyl group molar ratio, including the unreacted benzene, in the alkylate stream, is equal to or less than 1.5;
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sixth stream consisting of a transalkylate rich in monoethylbenzene; and

- 5 d) subjecting this sixth stream consisting of a transalkylate to at least one distillation-rectification to obtain a seventh stream consisting of ethylbenzene.
- 10 5. A process according to claims 1, 3, or 4, wherein the supported heteropolyacid catalyst comprises a supported phosphotungstic acid catalyst.
- 15 6. A process according to claims 1, 3, or 4, wherein the supported heteropolyacid catalyst comprises phosphotungstic acid on a silica support.
7. A process according to claims 1, 3, or 4, wherein the supported heteropolyacid catalyst comprises approximately 30% by weight phosphotungstic acid on a silica support.
- 20 8. A process according to claims 2, 3, or 4, wherein the Y zeolite catalyst is in the acid form.
- 25 9. A process according to any of the preceding claims, wherein the poly-ethylbenzene component includes di-, tri-, tetra- penta-, and/or hexa-ethylbenzene.
- 30 10. A process according to any of the preceding claims, wherein the benzene ring to ethyl group molar ratio in the alkylation reaction is equal to or less than 1.
11. A process according to any of the preceding claims, wherein the benzene ring to ethyl group molar ratio in the alkylation reaction is between 0.3 and 1.
- 35 12. A process according to any of the preceding claims, wherein the first stream also contains saturated hydrocarbons.

containing mono- and poly- isopropylbenzenes in which the benzene ring to propyl group molar ratio, including the unreacted benzene, in the alkylate stream, is equal to or less than 1.5;

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- b) subjecting this third stream consisting of an alkylate stream to at least one distillation/rectification to obtain a fourth stream which is a distillate containing poly-isopropylbenzenes;

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- c) transalkylating this fourth stream consisting of the distillate with a fifth stream consisting of benzene to obtain a sixth stream consisting of a transalkylate rich in cumene; and

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- d) subjecting this sixth stream consisting of a transalkylate to at least one distillation-rectification to obtain a seventh stream consisting of cumene.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/13100

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9320029	14-10-93	FR-A- 2689501	08-10-93
		AU-B- 3893193	08-11-93
		CA-A- 2133305	14-10-93
		EP-A- 0633872	18-01-95
		JP-T- 7501557	16-02-95
EP-A-402202	12-12-90	FR-A- 2648129	14-12-90
		AU-B- 632329	24-12-92
		AU-B- 5622490	13-12-90
		CA-A- 2018492	07-12-90
		DE-D- 69007683	05-05-94
		DE-T- 69007683	14-07-94
		ES-T- 2054291	01-08-94
		JP-A- 3031220	12-02-91
		US-A- 5177280	05-01-93
US-A-5177285	05-01-93	NONE	